I. X-RAY STRESS ANALYSIS AS APPLIED TO SOME WAR PROBLEMS.

II. X-RAY STUDIES OF KETONE 2-4 DINITROPHENYL-HYDRAZONES.

BY

THOMAS DAVID PARKS

B.S., Wheaton College, 1942

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1945

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ACKNOWLEDGMENT

The author wishes to express his appreciation to Professor G. L. Clark, under whose direction this work was carried out. His personal interest and inspiration have meant much in its successful completion.

Part I

X-RAY STRESS ANALYSIS AS APPLIED TO SOME WAR PROBLEMS

Introduction

The need of a simple non-destructive method of stress analysis in fabricated metal parts was early recognized, but not until comparatively recent years have claims been made for quantitative determination of stress by x-ray diffraction methods. Lester and Aborn (1) first studied line shift in diffraction patterns of metals under stress. Back reflection techniques with greater sensitivity was applied by many investigators (2-5). They worked with fine grained steels and claimed an accuracy which compared favorably with other methods of measurement. The purpose of this investigation was to test the applicability of these techniques to stress analysis in light metals, both cast and powder metal compacts.

Experimental

Three special pieces of equipment were required for the examination of cast Dowmetal H alloy. These were a pressure machine, a portable diffraction unit, and a precision rotating back-reflection camera.

Test bars were subjected to various stresses and back-reflection patterns were taken at each pressure. Very sharp lines were obtained at low pressures, but these became less distinct as the as the pressure was increased, until the specimen failed at a pressure of 42,100 psi. The diffraction lines which were obtained were progressively more diffuse and could be used as qualitative or semi-quantitative measure of stress in this particular alloy. A poor quantitative correlation was obtained for low stress values when aluminum powder was used as a calibrating substance and the line shift was measured.

A series of 4% copper-96% aluminum powder metal compacts were studied. They were pressed at pressures of 15, 30, 45, and 60 TSI and sintered at 590°C. No stress was observed by either transmission or back reflection examination in any of

the pieces. When precision powder patterns were taken of each of the specimens, a line shift was observed which suggested a progressive solution of copper in the aluminum with increasing pressure.

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Part II

X-RAY STUDIES OF KETONE 2-4 DINITROPHENYLHYDRAZONES

Introduction

2-4 dinitrophenylhydrazine was introduced simultaneously in Germany (1) and Italy (2) as a specific reagent for the characterization of carbonyl compounds. These two original investigations introduced a difficulty which is still of very great importance; the dimethyl ketone derivative was reported to melt at 114°C. and 128°C. Other investigators have found similar irregularities with other compounds in this series, and various explanations have been forthcoming. Campbell (3) claimed that discrepancies were due to the formation of impurities and that these impurities depended on the catalyst used in the reaction. He criticised the method of preparation of Brady (4) in which sulfuric acid was used as a catalyst. Allen (5), on the other hand, felt that the differences in melting points were too great to be caused by impurities. He suggested the possibility of different crystalline forms which he said were caused by cis-trans isomerism. However, three forms have been reported for furfuraldehyde 2-4 dinitrophenyldrazone (6), which is one more than can be explained by cis-trans isomerism, and two widely separated melting point values have already been pointed out for the derivative of dimethyl ketone.

An x-ray method of identification of a similar series of organic derivatives has been used in correlation with melting point data. McKinley (7) studied the phenyl isocyanate derivatives of

alkylated phenols and gives a table of d values with relative intensity data based on powder diffraction patterns.

The purpose of this investigation was to determine d values and intensities for the commonly used ketone derivatives of 2-4 dinitrophenylhydrazine, and to investigate the possible polymorphism of the dimethyl ketone derivative.

Experimental

2-4 dinitrophenylhydrazones of fifteen readily available ketones were prepared according to the method of Shriner and Fuson (8). They were purified by repeated recrystallization and, where possible, single crystals were grown. Two forms of the dimethyl ketone derivative were obtained when the compound was recrystallized from diethyl ether, and also when sulfuric acid was substituted for hydrochloric acid in the original preparation.

X-ray diffraction powder patterns were obtained on all of the derivatives, using filtered copper radiation. The master films serve as a qualitative method of identification of any of the ketones studied. The d values were calculated for the three most intense lines on each film and these were listed together with the relative intensities of each line. These data permit a qualitative analysis of these ketones without the use of the original films.

The crystal form of the dimethyl ketone derivative which melted at 128°C. was studied by powder, rotation about each axis, and Weissenberg projections. It was found to be triclinic and to be in space group $P_1^- \; C_1^i$ with the following constants.

$a_o = 7.12$ Å	$\alpha = 66°$
$b_o = 8.04$	$\beta = 86°$
$c_o = 9.91$	$\gamma = 102°$

The needle form of the same compound, which melted at 115°, did not lend itself to a complete single crystal study, but rotation was possible about one axis and the following constants obtained:

$a_o = 5.22$	
$b_o = 11.0$	$\alpha = 90°$
$c_o = 22.6$	

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Vita

The author was born in Alberta, Canada, on November 16, 1917. He obtained his elementary education in the public schools of Detroit, Michigan, and graduated from High School in New Westminster, British Columbia, in 1935. For the following three years he worked as a salesman for a wholesale stationer in Vancouver. In the Fall of 1938 he entered Wheaton College, graduating in June, 1942, with the degree of B.S. in Chemistry with honor.

He joined the University of Illinois Chemistry Department as an assistant in the Analytical Division in the Fall of 1942, which position he held until June, 1944, when he joined the Analytical section of the Rubber Program.

On June 19, 1943, he married Pauline Eliot Banford, and on January 16, 1945, they had a son, Daniel James.

He is a member of Sigma Xi, Sigma Pi Sigma, Chi Sigma Theta, The American Chemical Society, The American Society for Metals, and the American Scientific Affiliation. He is listed in *"Who's Who Among Students in Colleges and Universities."*

His publication is: (with G. L. Clark and C. W. Culmer) *"Measurement of Residual Lubricating Oil Thickness on Vertical Metal Surfaces"*, National Petroleum News, **36**, No. 49, R-875 (1944).

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